

NEXAFS from Grain Boundary Segregated Y and Zr in Alumina

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Introduction: Dopants Y and Zr at the level of 100 to 1000 ppm have been found to enhance alumina creep resistance at high temperatures by two orders of magnitude.^{1,2} We have made NEXAFS measurements on these materials to obtain information about local bonding of the dopants, which are known to be segregated to alumina grain boundaries.

Methods and Materials: Ultra-high purity α -Al₂O₃ was doped with Y₂O₃ at 100ppm and 1000ppm (Y/Al atomic ratio) levels, and with ZrO₂ at 100ppm level. Grain sizes were 0.5 μ m to 5 μ m. In the 1000ppm Y-doped sample, 80% of the Y is present as YAG. K-edge NEXAFS measurements for these samples were made with fluorescence detection. Transmission absorption measurements were made for metallic Y and Zr foils, Y₂O₃ powder, and ZrO₂ powder as standards. Results from some of these measurements are shown in Fig. 1.

Results: Grain boundary segregated Y and Zr show a positive chemical shift and the magnitude of the shift, as compared with that of Y₂O₃ and ZrO₂, respectively, is different for Y and Zr, indicating that, relative to Y₂O₃ and ZrO₂, charge transfers for the grain boundary segregated Y and Zr are different. This result is also supported by the strength of the threshold resonance. A pre-edge shoulder is seen in K edge XANES for grain boundary segregated Y and Zr but not for Y₂O₃ and monoclinic ZrO₂. This shoulder is attributed to the 1s \rightarrow 4d transition which is normally forbidden, but can occur because of d-p mixing which is favored by a tetrahedral coordination configuration. These results suggest that some of the grain boundary segregated Y and Zr have coordination configurations with tetrahedral symmetry. Although tetrahedral configuration does not necessarily require a coordination of four, it is consistent with EXAFS results^{3,4}, which indicate that the grain boundary segregated Y and Zr are under-coordinated compared with their respective oxides.

Conclusions: Atomic structural parameters obtained by EXAFS and XANES provide important parameters for computer calculations and modeling of the dopant segregated grain boundaries. More thorough interpretations of these spectra may be possible through molecular orbital calculations.

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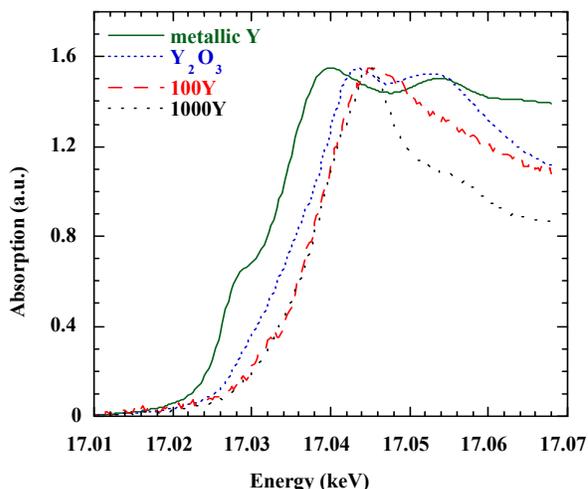


Figure 1. NEXAFS measurements for 100ppm and 1000ppm Y-doped alumina, Y₂O₃, and metallic Y.